TECHNICAL MEMORANDUM

From: Bruce Tiffany

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Re: King County Sanitary Sewer System - Characterization Sampling for Selected Phthalates •

and Benzyl Alcohol in the Lower Duwamish Basin - 2003 to 2006

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INTRODUCTION

As part of the Lower Duwamish Waterway cleanup process, the first Early Action sediment cleanup was conducted in 2003 and 2004 near the Duwamish/Diagonal Combined Sewer Overflow/Storm Drain (CSO/SD) outfall. The remediation of this site involved a combination of sediment removal followed by capping of the remaining sediment with clean material (EBDRP 2005).

The Duwamish/Diagonal CSO/SD outfall is estimated to discharge approximately 1,100 million gallons per year (MGY) of stormwater (Ecology 2004) and approximately 12 MGY of combined stormwater/sanitary wastewater from the Hanford #1 King County CSO (Hanford at Rainier). The east side of the Duwamish Siphon King County CSO also is located near the Duwamish/Diagonal CSO/SD outfall and is estimated to discharge approximately 2 MGY of combined stormwater/sanitary wastewater (King County 2006).

Following the remedial action at the Duwamish/Diagonal site, annual monitoring of surface sediments has occurred annually. This monitoring is conducted to evaluate the effectiveness of controlling upland sources to minimize or prevent the recontamination of site sediments. Results from the 2005 monitoring indicated that the sediments in the Duwamish/Diagonal Early Action Area were being recontaminated with benzyl alcohol (BA), benzyl butyl phthalate (BzBP), and bis-(2-ethylhexyl) phthalate (BEHP) (EBDRP 2007).

This sediment recontamination prompted King County to undertake sampling within the King County sewerage system to evaluate if there are locations in the system where these chemicals appear in greater amounts. This sampling involved looking at key nodes within the wastewater network. For this study, the key "nodes" in the system were located at King County wastewater pump stations. The results from these pump stations were compared with results from samples collected from the influent of King County's two large wastewater treatment plants. Discharges from industrial users of the King County sanitary sewer system also were evaluated to see if there are controllable sources of BA, BzBP, and BEHP. Industrial users were sampled in the Duwamish/Diagonal (Hanford #1) and Duwamish Siphon CSO basins. Results are also included for industrial users that are routinely sampled for semivolatile organic compounds (e.g., BA, BzBP and BEHP).

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Information on Target Chemicals

To provide background for this technical memorandum, information is presented on the characteristics and properties of BA, BzBP and BEHP. Except where noted, the Hazardous Substance Data Bank was the source of the information (HSDB 2007).

Benzyl Alcohol (BA)

- Sources: Used as a photographic developer, chemical intermediate, solvent and color developer in cosmetic products. Occurs naturally in flower oils and material exuded from trees. Reported concentrations in food: Non-alcoholic beverages 15 ppm; ice cream, ices. etc. 160 ppm; candy 47 ppm; baked goods 220 ppm; gelatins & puddings 21 to 45 ppm; chewing gum 1,200 ppm.
- Properties: Based on the high water solubility and the low coefficients for water-toorganic carbon partitioning (Koc) and water-to-octanol partitioning (Kow), BA is
 expected to be present primarily in the aqueous phase and not partition appreciably to
 organic carbon or non-aqueous phase liquids (NAPLs).
 - Solubility: 35,000 mg/L (at 20°C)
 - Koc = <5 to 15
 - Log Kow = 1.10

Benzyl Butyl Phthalate (BzBP)

- Sources: Used as a plasticizer and organic intermediate. Plasticizer for PVC-based flooring products, polyvinyl acetate emulsion adhesives, and other plastics.
- Properties: Particulate-phase BzBP is removed from the atmosphere by wet and dry
 deposition. In water, BzBP is expected to adsorb to sediment or particulate matter given
 its Koc value.
 - Solubility: 0.71 mg/L (temperature not specified)
 - Log Koc = ≥4.7
 - Log Kow = 4.91

Bis(2-Ethylhexyl) Phthalate (BEHP)

Sources: Approximately 95% of the BEHP produced is used as a plasticizer for PVC.
These products include wall coverings, tablecloths, floor tiles, furniture upholstery,
shower curtains, garden hoses, automobile upholstery, sheeting for wire and cable, and

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flexible tubing. Minor uses include solvent in erasable ink, cosmetics, vacuum pump oil, dielectric fluid for electrical transformers, and other uses (ATSDR 2002).

- Properties: BEHP will exist in both the vapor and particulate phases in the ambient atmosphere. Particulate-phase BEHP is removed from the atmosphere by wet and dry deposition.
 - Solubility: 0.284 mg/L (at 24°C)
 - Koc = 87,420 to 510,000 (Log Koc = 4.9 to 5.7)
 - Log Kow = 7.60

2006 SAMPLING OF KING COUNTY WASTEWATER TREATMENT PLANTS

The King County Wastewater Treatment Division conducts semi-annual sampling for a broad suite of parameters at its two large wastewater treatment plants – South (Renton) and West Point. These sampling events are required in the NPDES permits for the treatment plants. The sampling is scheduled to conduct one sampling event during the dry season and another during the wet season. Per sampling event, one 24-hour composite sample is collected at the West Point Freatment Plant and three consecutive days of 24-hour composite samples are collected at the South Treatment Plant.

The 2006 results for BA, BzBP, and BEHP are provided in Table A-1 in Appendix A. A summary of the results is provided in Table 1.

Benzyl Alcohol (BA)

The following ranges were observed per treatment plant:

- South: 20.8 to 63.9 μg/L and 12.2 to 30.0 lbs/day
- West Point: 23.0 to 75.3 μg/L and 33.8 to 52.3 lbs/day

Benzyl Butyl Phthalate (BzBP)

The following ranges were observed per treatment plant:

- South: 2.35 to 4.90 μg/L and 1.4 to 2.5 lbs/day
- West Point: 0.85 to 2.59 μg/L and 1.2 to 1.8 lbs/day

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Bis(2-Ethylhexyl) Phthalate (BEHP)

The following ranges were observed per treatment plant:

South: 10.4 to 13.9 μg/L and 5.6 to 9.0 lbs/day
 West Point: 4.61 to 13.7 μg/L and 6.8 to 9.5 lbs/day

To provide perspective to these results, residential/commercial monitoring data from EPA indicated a 0.02 to 22 μ g/L range for BEHP (EPA 2004).

2003 TO 2006 SAMPLING OF KING COUNTY PUMP STATIONS AND CSO LOCATIONS

In 2003 and 2004, the King County Industrial Waste Program collected wastewater samples at several King County wastewater pump stations that are tributary to the West Point wastewater treatment plant. These pump stations were selected to evaluate the BzBP and BEHP wastewater concentrations at three stations along the Lower Duwamish Waterway (E. Marginal Way PS, W. Marginal Way PS, Duwamish PS), one station located in a separated sanitary sewer service area (Matthews Park PS), and one station located in a combined stormwater/sanitary sewer service area (Interbay PS).

Sampling at each pump station occurred by collecting continuous 24-hour composite samples each day for approximately seven days. Separate sampling rounds were performed in dry and wet seasons to evaluate if dry or wet weather conditions impacted sample results.

At the beginning and end of each sampling round, equipment blank samples were collected from the automated sampling apparatus.

In February 2006, King County Industrial Waste Program staff collected wastewater samples at two CSO locations that are tributary to the Duwamish/Diagonal CSO/SD outfall. These CSO locations were the aftbay of the Duwamish Siphon and the Bayview/Hanford #1 discharge structure.

The 2003 to 2006 results for BzBP and BEHP are provided in **Table B-1** in **Appendix B**. A summary of the results is provided in **Table 2**.

Benzyl Butyl Phthalate (BzBP)

The following are the ranges and median values from the data collected (detects only):

- East Marginal Way PS: 0.6 4.0 μg/L, Median: 2.1 μg/L
- West Marginal Way PS: $1.0 7.3 \mu g/L$, Median: $2.4 \mu g/L$
- **Duwamish PS:** 0.9 69.8 μg/L, Median: 1.5 μg/L

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- Matthews Park PS: 1.1 1.9 μg/L, Median: 1.4 μg/L
- Interbay PS: 1.5 3.1 μg/L, Median: 2.0 μg/L
- Duwamish Siphon (Aftbay): 0.9 μg/L (one detected value)
- Bayview/Hanford #1: 1.2 2.0 μg/L

Results for BzBP ranged from a low of $0.6~\mu g/L$ (E. Marginal Way PS) to a high of $69.8~\mu g/L$ (Duwamish PS). Median BzBP values ranged from $1.4~\mu g/L$ (Matthews Park PS) to $2.4~\mu g/L$ (W. Marginal Way PS).

There was very little variability in the results from the residential service area (Matthews Park PS – Range: 1.1 to 1.9 μ g/L), slightly more variability in the combined service area (Interbay PS – Range: 1.5 to 3.1 μ g/L), and more variability in the more industrialized basins (E. Marginal Way PS – Range: 0.6 to 4.0 μ g/L; W. Marginal Way PS – Range: 1.0 to 7.3 μ g/L; Duwamish PS – Range: 0.9 to 69.8 μ g/L).

There was very little variability in the results obtained from dry weather and wet weather sampling events (see **Table B-1**).

Bis(2-Ethylhexyl) Phthalate (BEHP)

The following are the ranges and median values from the data collected:

- East Marginal Way PS: 1.6 35.0 μg/L, Median: 6.1 μg/L (Equipment Blanks: 0.8 6.0 μg/L)
- West Marginal Way PS: 8.7 148 μg/L, Median: 13.4 μg/L (Equipment Blanks: 1.1 10.9 μg/L)
- **Duwamish PS:** 7.3 39.5 μg/L, Median: 11.5 μg/L (Equipment Blanks: 1.0 13.5 μg/L)
- Matthews Park PS: 5.2 11.4 μg/L, Median: 8.2 μg/L (Equipment Blanks: 0.5 1.9 μg/L)
- Interbay PS: $7.1 26.3 \mu g/L$, Median: 10.0 $\mu g/L$ (Equipment Blanks: $0.79 6.03 \mu g/L$)
- Duwamish Siphon (Aftbay): 9.1 12.5 μg/L
- Bayview/Hanford #1: 6.4 ~ 8.1 μg/L

Results for BEHP ranged from a low of 1.6 μ g/L (E. Marginal Way PS) to a high of 148 μ g/L (W. Marginal Way PS). Median BEHP values ranged from 6.1 μ g/L (E. Marginal Way PS) to 13.4 μ g/L (W. Marginal Way PS).

There was very little variability in the results from the residential service area (Matthews Park PS – Range: $\underline{5.2}$ to 11.4 $\mu g/L$). There was more variability in the results from the E. Marginal Way PS (Range: 1.6 to 35 $\mu g/L$), but the mean and median results were the lowest of the five pump stations sampled. There was not a great deal of variability between the results from W. Marginal Way PS, Duwamish PS, and Interbay PS. The only outlier was a value of 148 $\mu g/L$ for

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the W. Marginal Way PS. Aside from this value, the value ranges from these three stations were fairly similar.

There was very little variability in the results obtained from dry weather and wet weather sampling events (see **Table B-1**).

The 2003 to 2004 sampling at the pump stations indicated significant problems with blank contamination. This was attributed to BEHP in the flexible tubing of the sampling apparatus. The associated sample results from these pump stations should be considered biased high for BEHP. For subsequent sampling events Teflon tubing was substituted for the flexible tubing.

2006 SAMPLING OF INDUSTRIAL USERS OF THE KING COUNTY SEWERAGE SYSTEM

In 2006 King County Industrial Waste Program staff collected samples from industrial users of the King County sewerage system, with an emphasis on industrial users located within Lower Duwamish Waterway CSO basins. The samples collected were analyzed for BA, BzBP and BEHP. **Appendix C** contains the following results from this sampling:

- Table C-1: Presents industrial users identified for sampling and sorted according to industrial category. Selected companies from different industrial categories were identified for sampling.
- Table C-2: Presents results for industrial users sorted by CSO basin.
- Table C-3: Presents results for industrial users sorted by industry type.

As presented in **Table C-1** a total of 57 industrial users were identified for study. Of these industrial users, 37 were identified for sampling. The companies identified for sampling are presented on **Figures 1** and **2** according to their Industrial Waste Program permit or discharge authorization number.

Tables C-2 and **C-3** present the results for BA, BzBP and BEHP. These results are further classified according to concentration, using the following categories per target chemical:

- BA: > 250 μg/L, >100 μg/L, <100 μg/L (Note: 2006 Treatment Plant Range = 20.8 · 75.3 μg/L)
- **BzBP:** $\geq 50 \ \mu g/L$, $\geq 10 \ \mu g/L$, $\leq 10 \ \mu g/L$ (Note: 2006 Treatment Plant Range = 0.85 4.9 $\mu g/L$)
- **BEHP**: > 100 μ g/L, >20 μ g/L, <20 μ g/L (Note: 2006 Treatment Plant Range = 4.61 13.9 μ g/L.)

Based on these categories, the following industries were identified per analtye:

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Benzyl Alcohol (BA)

Industrial Categories with BA < 100 µg/L:

Barrel Cleaning	Hospital
Boat/Shipyard	Metal Finishing
Cement/Readymix	Metal Recycling
Container Washing	Photo Processing
Decant Station (Vactor)	Pressure Washing
Food Processing	Rendering
Fuel - Bulk Storage	Solid Waste - Transfer Facility
Fueling Facility	Transportation Facility
General Type	Trucked Waste
Groundwater Remediation – Petroleum	Vehicle Washing

Industrial Categories with BA > 100 µg/L:

Centralized Waste Treatment	Paint Manufacturing
Laundry - Linen	
Industrial Categories with BA >250 µg/L:	
Laundry - Linen	

Benzyl Butyl Phthalate (BzBP)

Industrial Categories with BzBP < 10 µg/L:

Barrel Cleaning	Groundwater Remediation - Petroleum
Boat/Shipyard	Hospital
Cement/Readymix	Laundry – Linen
Centralized Waste Treatment	Metal Finishing
Container Washing	Metal Recycling
Decant Station (Vactor)	Photo Processing
Fuel Bulk Storage	Transportation Facility
Fueling Facility	Trucked Waste
General Type	Vehicle Washing

Industrial Categories with BzBP >10 µg/L:

Food Processing	Pressure Washing

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Pressure Washing	na e energi
Bis(2-Ethylhexyl) Phthalate (BEHP)	
Industrial Categories with BEHP <20 μg/L:	
Boat/Shipyard	Metal Recycling
Cement/Readymix	Paint Manufacturing
Centralized Waste Treatment	Photo Processing
Fuel – Bulk Storage	Solid Waste – Transfer Facility
Fueling Facility	Transportation Facility
Groundwater Remediation - Petroleum	Trucked Waste
Hospital	Vehicle Washing
Metal Finishing	
Industrial Categories with BEHP >20 µg/L:	
Barrel Cleaning	General Type
Container Washing	Laundry - Linen
Decant Station (Vactor)	Pressure Washing
Food Processing	Rendering
Industrial Categories with BEHP ≥100 μg/l	! <i>:</i>
Barrel Cleaning	General Type
Container Washing	Pressure Washing

For all of the industrial users sampled, flow rate information was collected for the day of sampling. This information was used, along with the reported target chemical concentration data from each industrial user, to estimate an aggregate industrial wastewater concentration. These data are presented in **Table 3**. Because of the difficulties of sampling all of these industries on the same day, this approach was used to estimate the industrial wastewater component. The following average values were calculated (detected results only):

- BA: $30.27 \mu g/L$ (Note: 2006 Treatment Plant Range = $20.8 75.3 \mu g/L$)
- BzBP: $0.81 \mu g/L$ (Note: 2006 Treatment Plant Range = $0.85 4.9 \mu g/L$)
- **BEHP**: 11.87 μg/L (Note: 2006 Treatment Plant Range = 4.61 13.9 μg/L)

[Total Industrial Discharge Rate: 1.034 million gallons per day (MGD)]

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To evaluate what these concentrations mean in the context of total loadings to the wastewater treatment plants, it is useful to compare the estimated total industrial loads with the influent wastewater loadings at the treatment plants. Since industrial users comprise less than 5% of the total wastewater flow to King County treatment plants, this figure is used as a conservative estimate of industrial flow. Using the treatment plant range of loadings from Table 1, a typical treatment plant influent flow rate of approximately 100 MGD, and assuming an industrial flow of 5.17 MGD (i.e., 5 x 1.034 MGD – again, a conservative estimate), the following are the calculated ranges of estimated percent loadings from the industrial users:

BA: 2 to 11%BzBP: 1 to 3%BEHP: 5 to 9%

Based on the results of this analysis, even if it were possible to completely eliminate the industrial loadings of BA, BzBP and BEHP from the influent of the wastewater treatment plants, there would still be significant loadings from non-controllable sources (e.g., domestic dischargers, etc.).

(Note: For the purpose of evaluating the effect of non-detected values on the aggregate industrial wastewater concentration, an exercise was conducted by inserting method detection limits (MDLs) for non-detected values. Since all non-detected values are some fraction below the associated MDL, this exercise produces a result with a known high-bias. Following this approach, the aggregate industrial wastewater concentrations for BA, BzBP and BEHP were 33.71 µg/L, 3.44 µg/L and 12.17 µg/L, respectively. All of these results were within the range of values from the 2006 sampling at the two large King County wastewater treatment plants; therefore, non-detected values are not expected to impact the finding that the industrial component for the target chemicals comprises approximately 10% or less of the total wastewater load to the two large King County wastewater treatment plants.)

Conclusion

The results of sampling industrial users for BA, BzBP and BBP indicate that, in aggregate, the industrial wastewater component is within the concentration range for wastewater received at the two large King County wastewater treatment plants. However, certain industries, although small in discharge volume, still need attention when conducting pretreatment inspections. The industries worthy of primary attention include the following:

- · Barrel Cleaning
- · Container Washing
- Pressure Washing

The chief concern with these facilities is to ensure that the wastestream receives adequate treatment for removal of oil and particulate matter. The typical pretreatment for these wastestreams would be the use of an oil-water separator or some form of gravitational settling.

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The primary mechanism being removal of particulate matter, since the selected phthalates generally adsorb to particulate matter – although solubility in oil also can be a concern.

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The industries of secondary concern include the following:

- · Laundries
- Food Processing

Both of these industries are difficult to control from a pretreatment perspective. Laundries and food processing facilities both use chemical products which are extremely difficult to remove from their respective wastestreams. As with other wastestreams, efforts to remove particulate material can be beneficial.

In conclusion, sampling in the King County sewerage system for BA, BzBP and BEHP did not indicate significant variability in the sample results. In particular, for BzBP and BEHP, there was little variability between combined and separated sewer service areas, domestic vs. industrial wastewater (as calculated from summation of loadings from individual dischargers), and dry vs. wet weather sampling. These target chemicals are ubiquitous in the environment. Although the continued application of standard pretreatment technologies can provide some degree of benefit, these alone will not be able to overcome the higher mass loading from domestic sources that are beyond the jurisdiction of a delegated pretreatment authority such as the King County Industrial Waste Program.

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FIGURES

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TABLES

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Table 1

2006 Range of Values Per Wastewater Treatment Plant - South (Renton) and West Point

Benzyl Alcohol - Min	20.8	ug/L	12.2 lbs/day
Benzyl Alcohol - Max	75.3	ug/L	52.3 lbs/day
	15.3%		
Benzyl Butyl Phthalate - Min	0.85	ug/L	1.2 lbs/day
Benzyl Butyl Phthalate - Max	4.9	ug/L	2.5 lbs/day
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Bis(2-Ethylhexyl)Phthalate - Min	4.61	ug/L	5.6 lbs/day
Bis(2-Ethylhexyl)Phthalate - Max	13.9	ug/L	9.5 lbs/day
Discharge Rate - Min			56.2 mgd
Discharge Rate - Max			176.2 mgd

Table 2

Summary of Pump Station and CSO Sampling for Bis-(2-

Ethylhexyl) Phthalate and Benzyl Butyl Phthalate

Bis-(2- Ethylhexyl) Phthalate	E. Marginal Way PS	W. Marginal Way PS	Duwamish PS	Matthews Park PS	Interbay PS	Duwamish Siphon (Aftbay)	Bayview/ Hanford #1
Minimum	1.6 µg/L	8.7 µg/L	7.3 µg/L	5.2 µg/L	7.1 µg/L	9.1 µg/L	6.4 µg/L
Maximum	35 µg/L	148 µg/L	39.5 µg/L	11.4 µg/L	26.3 µg/L	12.5 µg/L	8.1 µg/L
Mean	7.7 µg/L	20.3 μg/L	12.4 µg/L	8.3 µg/L	10.8 μg/L	11.0 µg/L	7.5 µg/L
Median	6.1 µg/L	13.4 µg/L	11.5 µg/L	8.1 µg/L	10.0 µg/L	-	- "
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N	26	26	24	18	17	3	4

Benzyl Butyl Phthalate	E. Marginal Way PS	W. Marginal Way PS	Duwamish PS	Matthews Park PS	Interbay PS	Duwamish Siphon (Aftbay)	Bayview/ Hanford #1
Minimum	0.6 µg/L	1.0 µg/L	0.9 µg/L	1.1 µg/L	1.5 µg/L	0.9 µg/L	1.2 µg/L
Maximum	4.0 µg/L	7.3 µg/L	69.8 µg/L	1.9 µg/L	3.1 µg/L	0.9 µg/L	2.0 µg/L
Mean	2.0 µg/L	2.5 µg/L	7.9 µg/L	1.4 µg/L	2.1 µg/L	0.9 µg/L	1.6 µg/L
Median	2.1 µg/L	2.4 µg/L	1.5 µg/L	1.4 µg/L	2.0 µg/L	-	-
N	19	15	22	18	18	1	4

Notes:

PS = Pump Station

Results collected from dry and wet weather sampling events.

Only detected values used in the analysis. No corrections made for non-detected values.

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Table 3

2006 Sampling of King County Industrial Users –
Summary of Results per Service Area

Industrial Users Sampled - West Side of Lower Duwamish Waterway (W)

Totals	VALUE	UNITS	LOADING, LBS/DAY	Average Ind. WW. µg/L
Benzyl Alcohol	-	-	2.58E-03	1.70
Benzyl Butyl Phthalate	-	-	2.61E-03	1.73
Bis(2- Ethylhexyl)Phthalate		-	1,60E-02	10.56
Discharge Rate	0.181	MGD		

Industrial Users Sampled - East Side of Lower Duwamish Waterway (E)

Totals	VALUE	UNITS	LOADING, LBS/DAY	Average Ind. WW.
Benzyl Alcohol	-	-	0.00E+00	0.00
Benzyl Butyl Phthalate	-	-	1.62E-03	6.34
Bis(2- Ethylhexyl)Phthalate	<u> </u>	-	2.46E-02	96.42
Discharge Rate	0.031	MGD		

Industrial Users Sampled - East Side of Lower Duwamish Waterway - Tributary to KC CSO (E/KC CSO)

Totals	VALUE	UNITS	LOADING, LBS/DAY	Average Ind. WW.
Benzyl Alcohol	-	-	2.17E-01	53.18
Benzyl Butyl Phthalate		-	2.80E-03	0.69
Bis(2- Ethylhexyl)Phthalate	_	-	5.04E-02	12.35
Discharge Rate	0.489	MGD		

Industrial Users Sampled - Outside Lower Duwamish Waterway

Totals	VALUE	UNITS	LOADING, LBS/DAY	Average Ind. WW, μg/L
Benzyl Alcohol	-	-	4.14E-02	14.92
Benzyl Butyl Phthalate	-		0.00E+00	0.00
Bis(2- Ethylhexyl)Phthalate		-	1.14E-02	4.12
Discharge Rate	0.333	MGD		

Summation of Industrial Users Sampled

<u>Totals</u>	VALUE	UNITS	LOADING, LBS/DAY	Average Ind. WW,
Benzyl Alcohol	-	-	2.61E-01	30.27
Benzyl Butyl Phthalate	-	-	7.03E-03	0.81
Bis(2- Ethylhexyl)Phthalate	_	-	1.02E-01	11.87
Discharge Rate	1.034	MGD		

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APPENDIX A 2006 NPDES PERMIT DATA FOR SOUTH (RENTON) AND WEST POINT TREATMENT PLANTS

APPENDIX B SANITARY SEWER CHARACTERIZATION SAMPLING FOR PHTHALATES

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APPENDIX C KING COUNTY INDUSTRIAL WASTE PROGRAM – 2006 SAMPLING OF SANITARY SEWER INDUSTRIAL USERS

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